INSTITUTE NOTES.

OCTOBER 1940.

MEMBERS SERVING WITH H.M. FORCES.

The following is the first list of members of the Institute who are serving with H.M. Forces. The information is correct to the date of notification, though incomplete. Promotions and transfers may have been made subsequently. The Secretary will be pleased to receive additional information from time to time both as regards members in this list and members from whom information has not yet been received. Such additional information will be incorporated in a subsequent list.

Adlington, R. E., Capt., R.A.S.C.
Bartley, E. B., Cadet.
Blake-Smith, C., Flight-Lieut., R.A.F.
Boshell, E. G., R.A.F.
Bowker, T. D.
Brown, C. Barrington, Capt.
Chisholm, R. A., Flying Officer, R.A.F.
Clark, L. V. W., Lieut.-Col., R.A.O.C.
Collins, W. T., Capt.
Downs, W. W., Eng.-Commander, R.N.R.
Edwards, G. N. P., L/Cpl., R.E.
Farquharson, D. I., Flight.-Lieut., R.A.F.
Gould, G. C., Capt.
Green, R. L., Capt., R.A.
Hastings, H. W.
Heseltine, G. R. N., Lieut.-Col., M.C., Honourable Artillery Company.
Jackson, G. G., Lieut.
Janion, L. P., Sapper, R.E.A.A.
Laycock, V., Capt., R.A.S.C.
Marshall, R. W., Major.
Mason-Pay, P. A., 2nd London Scottish Regt.
Medlicott, H. E., D.S.O., Lieut.-Col., H.Q. Staff.
Moore, J. L., 2nd Lieut., R.A.
Patrick, J. S., Lieut., R.A.O.C.
Pidgeon, D. G., 2nd Lieut., R.A.S.C.
Plaskow, C. S., R.A.F.
Proctor, R. H., L/Cpl., R.E.
Provest, T. G., Capt.
Ramsay-Smith, D. L., R.A.F.
Robinson, A. W., 2nd Lieut., R.A.S.C.
Robinson, J. B., Cadet, O.C.T.U.
Rowntree, W. B., Capt., R.E.
Smellie, J. R., R.N.V.R.
Stephenson, F.
Steuart, W. O., A.A. Regt., R.A.

AWARD OF THE GEORGE MEDAL.

The Council warmly congratulates Mr. WILLIAM SIGSWORTH, A.M.Inst.Pet., on being among the first recipients of the award of the George Medal for conspicuous gallantry.

INSTITUTE SCHOLARSHIP.

The Council has awarded an Institute Scholarship of £40 per annum tenable at the Imperial College of Science and Technology to Mr. GEOFFREY JARDINE CLARKE, Stud.Inst.Pet. (Royal School of Mines), for the year 1940–41.

PAPERS FOR THE *JOURNAL*.

Owing to the war, work on a number of papers which were under preparation for the *Journal* or meetings of the Institute has had to be suspended. The Honorary Editor and the Publication Committee will therefore welcome the submission by members of papers suitable for publication in the *Journal*. The condition on which papers are printed is that they shall be approved by a referee appointed by the Publication Committee and subsequently by the Censorship Bureau of the Ministry of Information.

ARTHUR W. EASTLAKE,
Honorary Secretary.

INSTITUTE MEETINGS.

It has not been possible to arrange the customary programme of meetings of the Institute in London for the first part of the 1940–41 Session. Informal meetings or luncheon meetings may be held, and separate notification of these will be sent to all members residing in the London and Home Counties area as and when they are arranged.

If circumstances permit, preprints of papers to be published in the *Journal* will be circulated for written discussion.

BRANCH NOTES.

MEETING OF U.S.A. MEMBERS.

Members of the Institute in U.S.A. are holding their Annual Dinner and Meeting at the Stevens Hotel, Chicago, on Wednesday, 13th November. Mr. T. A. Boyd, Director of Research, General Motors Corporation, will be the speaker.

Stanlow Branch.

The following programme of meetings of the Stanlow Branch has been provisionally arranged for the first part of the 1940–41 Session:

Wednesday, 23rd October — **Friction and Lubrication.** by J. E. Southcombe.
Wednesday, 13th November — Subject to be arranged.
Wednesday, 11th December — **Automatic Instruments in Petroleum Refining,** by D. J. Pull.
January 1941 — Address by the President, Prof. A. W. Nash.

Informal meetings, at which short lectures, followed by discussion, will be the rule, will be arranged as opportunity offers.

Enquiries regarding the activities of the Stanlow Branch should be addressed to the Hon. Secretary: Mr. J. C. Wood-Mallock, Lobitos Oilfields Refinery, Ellesmere Port, Cheshire.

Birmingham Students' Section.

The Annual General Meeting of the Birmingham Students' Section was held at the University on 9th October. The following were elected officers and committee of the Section for the year 1940–41:

Chairman: V. D. Daft.
Vice-Chairman: H. A. Cheetham.
Hon. Secretary and Treasurer: Dr. A. H. Nissan.
Committee: I. A. Willmott, G. Buxton, J. R. Over.

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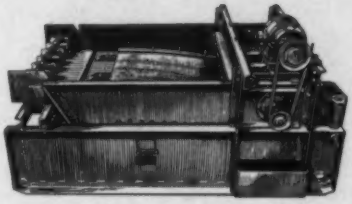

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Vol. 26. No. 204. October 1940.

CONTROL OF DRILLING MUD IN THE FIELD.*

By H. C. H. Darley, B.Sc., A.M.Inst.Pet.

Introduction.

The laws governing the chemical and physical properties of mud are not yet fully known, and much research work continues to be done on the subject. Most of us on the field have little time for research and must apply the results of others to the practical problems encountered in handling mud. This paper therefore formulates no new theory, but aims at presenting a means of testing muds which will give rapid and comparative results, and at establishing from these some system of treatment and control.

Flow Characteristics of Mud.

The essential flow characteristics of mud were clearly demonstrated by P. H. Jones and E. C. Babson [1] using a MacMichael type viscometer. With this type of viscometer mud is rotated at various speeds in a cup. An open-ended cylinder is suspended in the mud on a torsion wire. The deflection of this cylinder gives a measure of the resistance to shear of the mud at any instant.

Very briefly their results were as follows :—

If a thixotropic mud is sheared at a given speed, it will gradually assume a deflection typical of that speed, irrespective of its previous state of shear. This value is attained when equilibrium is established between the gelling and disrupting forces. If a mud is sheared to equilibrium at a given speed and the rate of shear then reduced, the initial deflections at each successive lower rate of shear will give a straight line which will, if projected, cut the axis above zero. The slope of this line is called by these workers the "immobility," and the value at which it cuts the axis the "yield point" (see Figs. 1 and 2). Since they are determined before thixotropy can have any effect, immobility and yield point are typical of the rate at which the mud was originally sheared to equilibrium. To define the flow characteristics of a mud, yield point expressed in dynes/cm.^{2} and immobility in centipoises for several rates of shear are given.

The author made some similar but more approximate experiments on drilling muds taken from Apex Wells. A synchronous motor was used to stir the mud at a fixed rate by driving a paddle in a cup fitted with baffles. Two speeds were obtained through gears. The cup had a capillary tube fitted to the bottom. In the first series of experiments the length of time required to shear a mud to its equilibrium value at each speed was found by stopping the paddle every minute and timing the discharge rate through the capillary tube. The discharge rate was then plotted against length of time sheared. Over a number of muds the time required to reach approximate equilibrium was found to vary from 10 minutes to more than half an hour. Examples of each type are given in Fig. 3.

* Paper read to a meeting of the Trinidad Branch on 1st May, 1940.

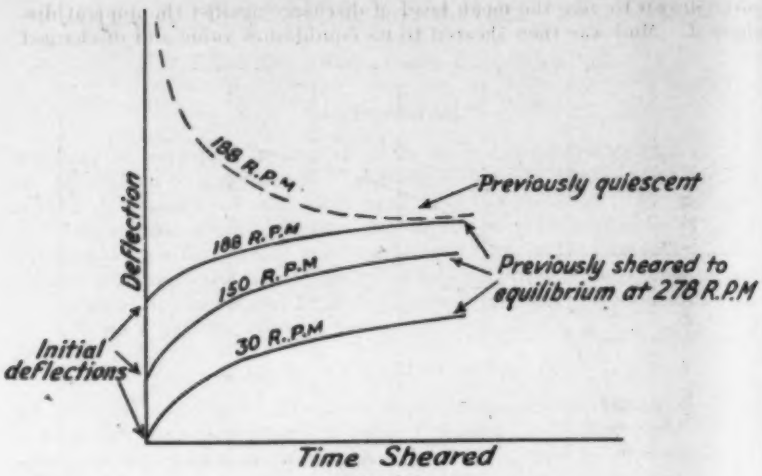

188 R.P.M
Previously quiescent
Deflection
188 R.P.M
150 R.P.M
Previously sheared to
equilibrium at 278 R.P.M
30 R.P.M
Initial
deflections
Time Sheared

FIG. 1.

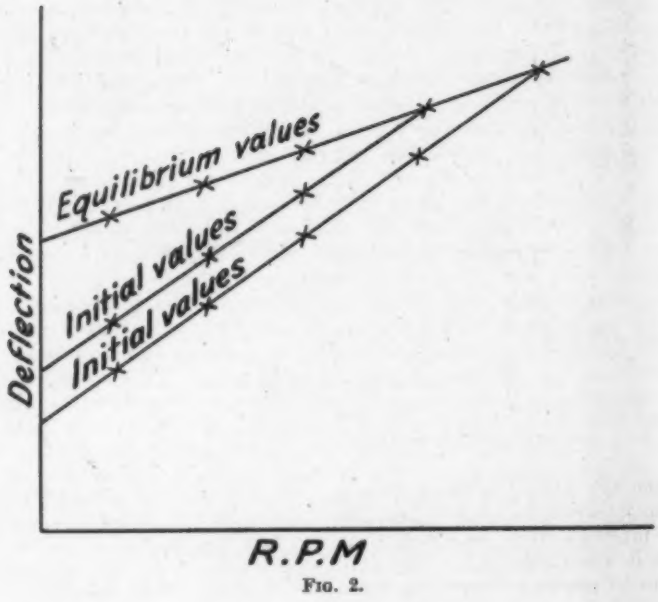

Equilibrium values
Initial values
Initial values
Deflection
R.P.M

FIG. 2.

In the second series of experiments the cup was first calibrated and a curve drawn to give the mean head of discharge against the amount discharged. Mud was then sheared to its equilibrium value and discharged

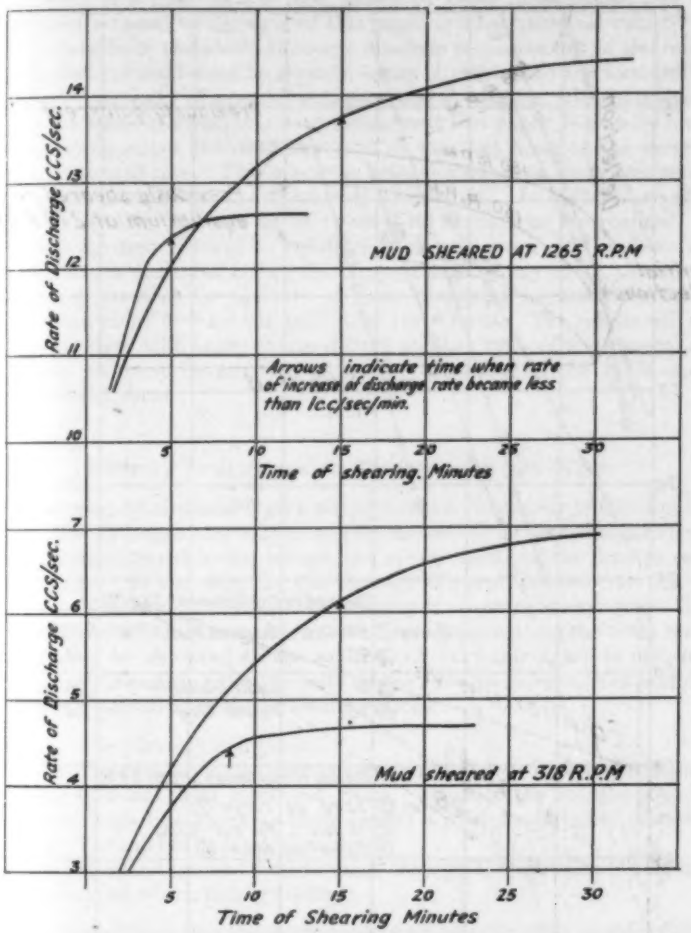


FIG. 3.

VARIATION OF VISCOSITY OF MUD WITH TIME OF SHEARING.

continuously into a graduated cylinder. The time at which the level passed certain intervals was noted, and thus the discharge rate between each of these intervals could be obtained and plotted against the mean head at which it was discharged. The whole cup seldom took more than half a minute to discharge, and thixotropy was consequently negligible. The

method is rough, and it is necessary to take the mean of about six sets of readings to get reasonably accurate results.

Some typical results are shown in Fig. 4. The slope of a line is a repre-

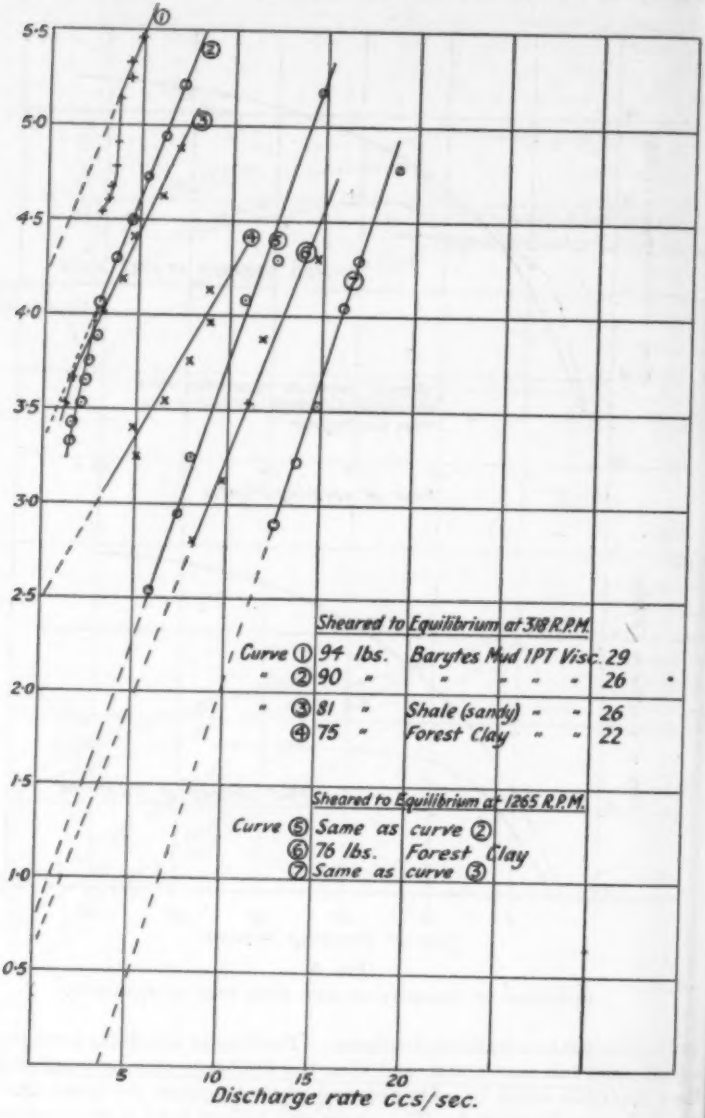


FIG. 4.

VARIATION OF RATE OF DISCHARGE OF MUD WITH HEAD.

sentation of the immobility. The point at which a line cuts the axis indicates the yield point for the previous rate of shear. It can be seen that at low rates of shear the curve leaves the straight line. This is probably due to plug flow setting in. There is, of course, actually no sharply defined yield point of a mud, as has been shown by other instruments, and the yield point referred to throughout this paper is a hypothetical value.

It is clear from the above that any absolute measurement of the resistance to shear of mud must be given in terms of yield point and immobility. The term " viscosity of a mud," as understood in common oil-field language and in the sense in which it is used throughout this paper, is usually found by measuring either the discharge rate at constant head or the shearing force at constant rate. This gives the total resistance to shear comprising yield point, immobility, and frequently thixotropy. It is therefore often highly misleading, but can be of value if its limitations are realized. If the muds are first reduced to equilibrium at any given rate of shear and the viscosity is measured before thixotropy can have any effect, the results will be comparative for the rate of shear obtaining immediately before the measurement and for the particular instrument. The results will not be comparative with those obtained from another type of instrument, nor will they give any information as to the behaviour of the muds under other rates of shear.

Routine Evaluation of Viscosity at the Well.

This is usually obtained from a simple rugged viscometer of the capillary type. The principal object is to enable the driller to obtain some idea of the resistance offered to the pumps and of the ability of the mud to carry up cuttings. As the mud travels through the well its velocity changes over wide limits, and therefore its viscosity is constantly changing. It is impossible by any means to arrive at a figure representing the total resistance offered by the mud to the pumps. A very fair figure is obtained, however, by measuring the viscosity of the mud as it leaves the annulus. This point is chosen for the following reasons :—

1. The viscosity is highest.
2. The resistance to shear in an annulus is very high. With 3-inch pipe in 6-inch hole Reid and Evans [2] estimate the resistance in the annular space at about six times that of a pipe of equivalent diameter.
3. The mud is in streamline flow.
4. The mud has had time to reach the equilibrium value for the rate of shear at which it is travelling.

It has been shown that the single-reading viscometer gives no information about the behaviour of the mud at any rate of shear but that of measurement. It is therefore obvious that the viscometer must be so designed that the velocities through the capillary correspond approximately to those obtaining in the annulus. (This must of necessity be approximate, since flow conditions in the capillary tube and the annulus have not yet been properly correlated.) Further, the sample must be taken and measured in a very short space of time if thixotropy is not to alter the

results. The local I.P.T. viscometer * does not satisfactorily fulfil either of these requirements. It is somewhat slow in use and the velocity through the orifice appears to be on the high side. Because of the latter defect it is inclined to give comparatively low readings with high gel muds. The most obvious example of this is cement-cut muds. A reduction in head would remedy both these defects.

It is useful at the well to take a viscosity of the mud entering the well after degassing. The difference between the two viscosities is a rough measurement of the thixotropy.

Routine Viscosity Determinations in the Laboratory.

The object of these is more to find out something of the properties of the mud with a view to controlling it, rather than the actual resistance to shear at the well. There are two opposing factors to be considered: time and accuracy of results. If time is no object, a viscometer like the Mac-Michael, giving both yield point and immobility, should unquestionably be used.

For quicker results a single-shot instrument may be used, but, as pointed out previously, the results are of limited value. The mud must first be reduced to equilibrium at some standard rate of shear. The most suitable rate of shear will be an approximation to that usually prevailing in the annulus, and viscosities through the capillary should be of the same order.

A suitable viscometer of this type is the capillary cup with the mud previously stirred by a motor-driven paddle. A gear-box will allow for two speeds, which can be selected by experiment to give rates of shear similar to "ingoing" and "outgoing" mud.

The largest source of error in this method is the correction for specific gravity of the mud. To obtain comparable results all readings must be corrected to a standard head. This cannot be done accurately unless immobility slopes are known. With similar types of mud such as may be obtained on one field, immobility slopes may differ little enough to allow a single slope to be assumed, and the correction then becomes:—

$$r = r_1 + (H - H_1) \tan. \theta$$

when r is discharge rate at head H
r_1 is discharge rate at head H_1
and θ is the immobility.

An approximation necessary on account of time is the equilibrium value, there being insufficient time to shear the mud until its viscosity is really constant. The mud must therefore be sheared until the rate of change of viscosity falls below a certain standard.

It can be seen from the above that with the limited time available for routine tests viscosity readings must remain an approximation with a limited application.

* This is a viscometer of the Marsh type designed to meet Trinidad conditions as a result of discussion between interested members of the local I.P. Branch.

Classification of Muds.

The particles comprising a mud may be divided into two groups: suspensory, *i.e.*, those which would suspend themselves if isolated and made up into a separate suspension—and suspensoids, which are those that would not. This classification is somewhat indefinite, because the ability of particles to suspend themselves is affected by their concentration. Further, the division between suspension and deposition is by no means sharp, and time must always be taken into account. But while there is a group of particles the classification of which is uncertain, the great majority fall clearly into one or other of the groups.

If a suspensoid mud is diluted by two or three times its volume with water, then the particles which are immediately deposited are suspensoids. This analysis is rough, but simple and quick. The use of the term suspensoid is perhaps unfortunate in view of the fact that many workers use it to denote a hydrophobic sol.

The suspensory group is mainly composed of particles of colloidal dimensions. These can be classified as hydrophilic or gel-forming colloids and hydrophobic colloids. The distinction between the two is very marked. Hydrophilic colloids give a very much more rapid rise in viscosity with increasing concentration. They are also responsible for the thixotropy, including, of course, the formation of gels. It is therefore to be expected that they will have a predominating effect on the mud, and the proportion and properties of those present are the main factors in determining its behaviour.

The suspensoid group consists broadly of inert particles of clay, sand, and barytes of dimensions greater than colloidal. Their effect on the viscosity of a suspension is relatively small, but increases with their concentration until they eventually form a mechanical structure. The particle size of suspensoids largely determines their effect on the viscosity of a suspension. (See Reid and Evans [2]—"Drilling Mud.")

The behaviour of a mud can be controlled by its composition. The necessary viscosity for the primary functions is best supplied by gel-forming colloids, because of their thixotropic nature. On the other hand, too high a concentration is highly undesirable, because of the high viscosity involved. Suspensoids are only desirable in a mud to supply weight. Hence their specific gravity should be as high as possible. The greater their particle size the less their effect on the viscosity, but particle size is limited by two factors. In the first place, a balance must be struck between particle size and the concentration of gel-forming colloids necessary for suspension. In the second place, too large a particle size will cause too much abrasion.

Now, it has been seen that the viscosity of a mud is a somewhat difficult thing to determine, and even when determined it gives only limited information about the mud. If a simile may be used, a high viscosity is like the temperature of a sick man: it shows that he is ill, but does not say what is wrong with him. Since the properties of a mud must be determined by its composition, much fuller information about all aspects of its behaviour can be obtained from an analysis. The author has used a limited form of classification which has given good results with the similar types of mud such as are obtained from one field. In this system unloaded clay muds are

classified according to the ratio of the viscosity to the percentage of solids by volume. This ratio is the essence of the classification, because, since the particle-size distribution of the suspensoids of the normal drilling muds is very much the same, it is an indication of the colloidal properties, the higher the viscosity for a given amount of solids, the greater the strength of the gel-forming colloids. It is also held that the action of the gel-forming colloids is the basic factor in determining the behaviour of the mud. A

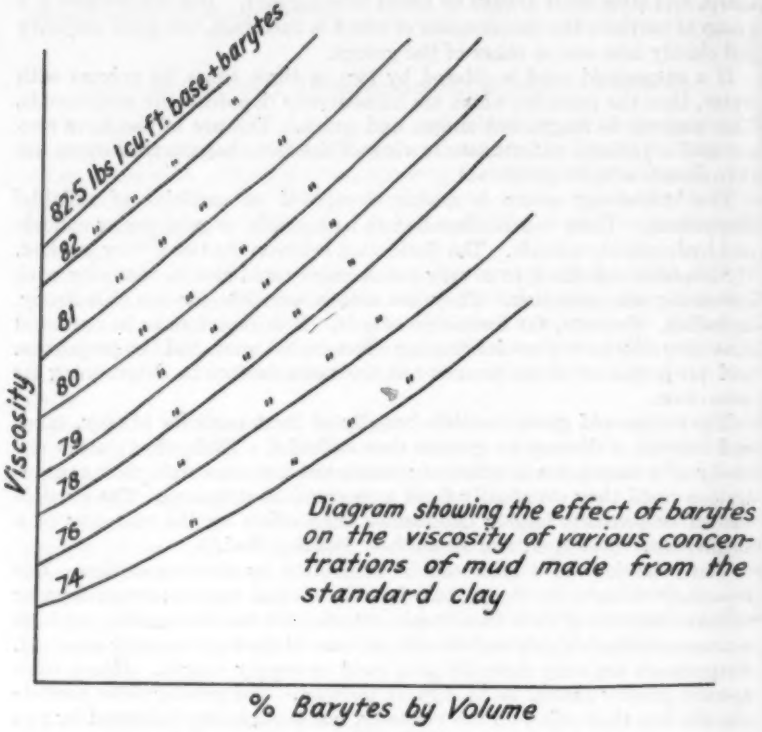


Diagram showing the effect of barytes on the viscosity of various concentrations of mud made from the standard clay

FIG. 5.

simple way to express results is to select some clay as standard and measure its viscosity at various concentrations. The viscosity of a test clay is then compared with these, and the concentration of the standard clay required to give the same viscosity as the test clay will be a comparison of their colloidal properties. Thus a 80–77 lb./cu. ft. clay means a mud weighing 80 lb./cu. ft. the viscosity of which is the same as a 77 lb./cu. ft. mud of the standard clay. Since these two figures give an expression for the concentration and nature of the suspension, quite a good opinion may be formed of its behaviour.

If the mud contains barytes it must be analysed and considered as two

components, the clay mud as the base and the barytes. The mud is first evaporated to dryness and the specific gravity of the solids determined. The total percentage of solids by volume in the original mud is then calculated, and from it and the weight per cu. ft. the clay base can be easily calculated or obtained from a chart. The concentration of the clay base being thus determined, it remains to obtain a measure of its colloidal properties. In a previous experiment various concentrations of the same standard clay were loaded with various amounts of barytes and the viscosity taken in each case. A curve of viscosity against barytes content was then drawn for each concentration of the clay base (Fig. 5). When testing a mud, its viscosity is found, and the amount of barytes it contains is obtained from the above analysis. The equivalent clay base of the standard clay is the one which gives the same viscosity as the test mud for the same percentage of barytes. The ratio of the concentration of clay base of the test mud to the equivalent standard clay base is a comparison of their colloidal properties. The results are expressed as before. Thus a 100–80–77 lb./cu. ft. mud means a mud weighing 100 lb./cu. ft. If all the barytes were removed it would weigh 80 lb./cu. ft. and would have the same viscosity as a 77 lb./cu. ft. standard clay mud.

The author has used this system on daily samples from drilling wells with satisfactory results. The main difficulty is that, to yield comparative results, the muds should all be in the same electro-chemical condition, whereas, of course, the muds came in from the wells in varying stages of chemical treatment. The only way to overcome this difficulty is to treat the mud with the usual reagents and use the lowest viscosity that can be obtained. In preparing the curves, the standard clay was, of course, similarly treated. While this probably does not always give strictly comparative figures for the actual composition of the mud, yet as a practical means of predicting the behaviour of muds it works out very well.

For the sake of convenience in drawing graphs and compiling records the author uses the ratio of the percentage solids in the equivalent standard clay base to that in the test clay base as an indication of the colloidal properties. This ratio has been called the "colloidal index," and the higher it is the higher is the proportion of gel-forming colloids. It is not a very satisfactory term, because, if a mud is diluted and tested at various stages of dilution, its colloidal index changes. This is primarily due to the shape of the viscosity–concentration curves.

Since thixotropy also depends mainly on the amount of the gel-forming colloids present, it is reasonable to expect some kind of relationship between it and the colloidal index. Fig. 6 shows the thixotropy and colloidal index taken directly from the results of a number of consecutive daily tests. An exact correlation cannot be expected in view of the other factors involved. The principal one of these is the fact that the thixotropy was measured in all stages of chemical treatment, whereas the colloidal index was determined after the optimum dose had been added.

Fig. 7 shows how the general level of the viscosities at the well are dependent on the clay base and the colloidal index. The viscosity in each case was taken by averaging the viscosities recorded by the drillers during the 12 hours before and after the sample was taken. The samples included all types of mud up to about 105 lb./cu. ft. The higher weights cannot be

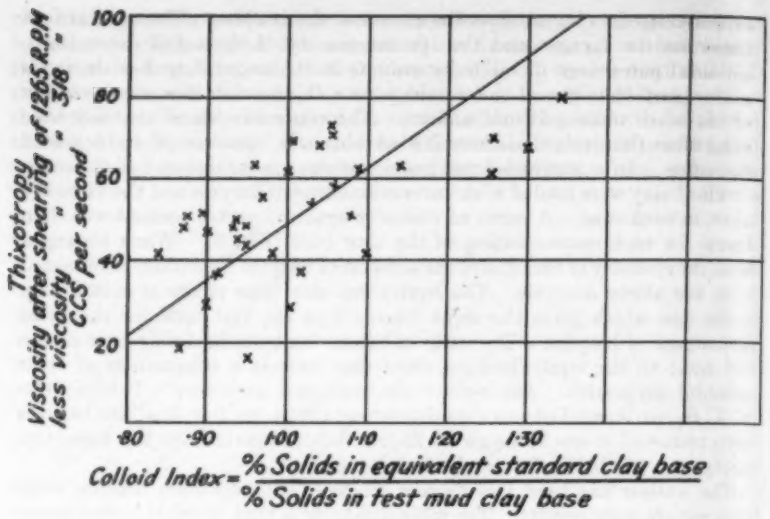


FIG. 6.

GRAPH SHOWING EFFECT OF THE COLLOIDAL PROPERTIES OF THE CLAY BASE ON THE THIXOTROPY OF A MUD.

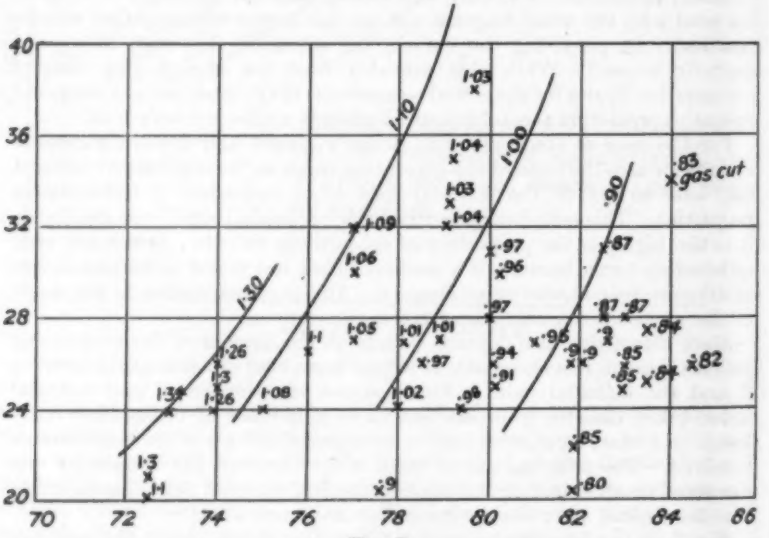


FIG. 7.

GRAPH SHOWING THE EFFECT OF CLAY BASE AND ITS COLLOIDAL PROPERTIES ON THE GENERAL LEVEL OF VISCOSITY AT THE WELL.

Figures on the chart are the colloidal index which is

$$\frac{\%\ \text{Solids in the equivalent standard clay base}}{\%\ \text{Solids in the test mud clay base}}.$$

Lines represent muds of equal colloidal index.

expected to give good correlation, since the driller's viscosities are not corrected for specific gravity. It can be seen how the muds of higher colloidal index give higher viscosities for the same weight per cu. ft. or, more clearly, how the same viscosity is given by much higher concentrations of clays of lower colloidal index. Considering the number of variables not allowed for, the correlation is striking, and is the best proof the author can offer of the validity of this system of classification.

The "in" viscosity and gel strength must also depend on the clay base and colloidal index, and it has been proved by field experience that the tendency to "gas-cut" depends on them. It is also hoped to establish a relationship with the wall-building properties.

It is therefore suggested that a fairly complete picture of a mud may be gained even by this rather approximate system of analysis, and that any aspect of the behaviour of the mud may be judged from the results. Experience with this system suggests the feasibility of control by a more complete hydraulic analysis, without using direct viscosity measurements except those taken by the driller. A fairly rapid analysis into two or more suspensoid groups and a more truly colloidal suspension should present no serious practical difficulty. The concentration and viscosity–concentration ratio of this suspension would be the dominating factor in the behaviour of the mud. With moderately dilute colloidal suspensions most of the difficulties of viscosity measurements would be removed. From the experience gained with the present system of analysis it seems likely that the results would be a trustworthy basis on which to judge the performance of the mud at the well, but of course much data would have to be collected to confirm this.

Control.

Many articles and papers appear on various phases of the subject of mud, but the author has not yet come upon one giving details for a system of mud control. Therefore a brief outline of the method used on the Apex field is given for what it is worth.

Daily samples are brought into the laboratory from the drilling wells. The viscosity at speeds corresponding to the "in" and "out" viscosities at the well are taken on the motor-driven paddle viscometer as previously described. The effect of chemical reagents is tried at the fast rate of rotation because the results are obtained much quicker. Quebracho and caustic soda solution, usually in the ratio 1·6 to 1·0, is the most common reagent. Silicate of soda is sometimes used, and good results are now being obtained from compounds containing complex phosphates. The gravity is determined by hydrometer, and a rough figure is obtained for sand content by dilution and settling. A figure for gas entrained in the mud is determined by taking a fixed volume in a special density cup, adding a measured amount of water, shaking up and allowing the gas to escape. The density cup is again filled with the diluted mud and weighed. From the proportion of water added it can easily be calculated what the original weight of the mud would have been had there been no gas in it, and the difference between this and the actual weight is an approximate measure of the amount of gas in the mud. The diluted mud from the density cup

is then evaporated rapidly to dryness and again weighed. The loss of weight gives the volume of water and by difference the volume of the solids, and hence their specific gravity. From these results the clay base and the colloidal index are ascertained. All results are recorded and a daily graph is kept of the more important factors, including the results obtained at the well.

The driller is provided with the local I.P.T. viscometer and a mud scale. He takes readings at frequent intervals. Whenever the viscosity rises above a given figure he adds a "dose" to the mud. This is repeated when the viscosity rises again. This "dose" is fixed on the results of the laboratory tests described above and is changed from time to time as conditions change. It usually consists of a stated amount of chemical reagent and water. The water is measured in by means of a simple constant-head meter discharging through interchangeable chokes. The "dose" is added over the period of one circulation.

The "dose" is determined as follows: In normal circumstances the optimum amount of chemical reagent is put in with each dose. This amount is judged from the laboratory test and past experience. If subsequent tests show the amount too much or too little, it is adjusted accordingly. The amount of water depends entirely on the clay base and whether it is desirable to allow it to rise or to fall.

The general aim is to allow the base to rise as much as possible, in order to save barytes. Much more data need to be collected before it can be decided to what limit it is economical to allow the base to rise. It must obviously depend largely on the drilling conditions and the nature of the clay base. At the moment, lower bases are held for muds of high colloidal indices because of the higher "out" viscosities (see Fig. 7) and the greater tendency to gas-cut.

Careful control of the clay base has been found to yield considerable economies in the use of barytes. This is believed to be due to the fact that high viscosities are avoided. As soon as the viscosity rises above a given figure, the driller treats the mud. Clay-base control merely represents a system whereby the minimum amount of water is used to keep within the desired range of viscosities. Low viscosities are economical because with them less solids are picked up and dispersed through the mud and, more important, there is less tendency to gas-cut. (This does not take into account the many advantages of low viscosity to the driller. That viscosity can very materially affect the speed of drilling, especially in deep holes, has been proved several times on the Apex field.) That low viscosities are economical in barytes consumption is shown in Fig. 8, which gives the barytes used to maintain weight in wells before and after the policy was introduced in full on the Apex field.

Blow-outs and Gas-cutting.

The connection between blow-outs and gas-cutting is a point which needs emphasizing. With most blow-outs it can be shown that the reservoir pressure did not exceed that of the hydrostatic head of mud of the gravity that was being maintained, or even that of water. Therefore the blow-out

must have been preceded by gas-cutting, without which it would not have occurred. Such gas-cutting can take place merely from the gas in the sand cut by the bit. Also it must be remembered that gas will tend to

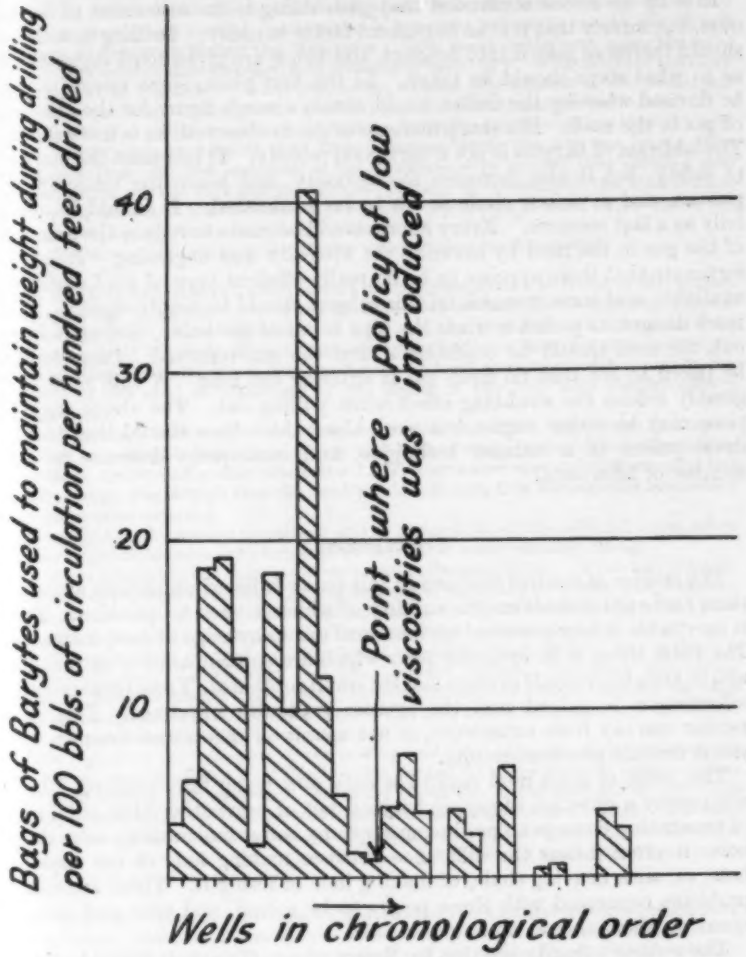

Bags of Barytes used to maintain weight during drilling per 100 bbls. of circulation per hundred feet drilled
40
30
20
10
Point where viscosities policy of low was introduced
Wells in chronological order

FIG. 8.

DIAGRAMMATIC REPRESENTATION OF THE AMOUNT OF BARYTES USED TO MAINTAIN WEIGHT IN INDIVIDUAL WELLS.

seep into the mud from sands already penetrated, because of the difference in specific gravity between it and the mud. This will not be controlled by the difference in pressure between the gas and mud column, but by

the formation and maintenance of a good mud sheath on the face of the sand. It is significant that blow-outs often occur a long time after the sand has been penetrated, and frequently when out of the hole when conditions for gas-cutting are optimum.

It is by no means contended that gas-cutting is the sole cause of blow-outs, but merely that it is an important factor in many. Drilling technique should therefore take it into account, and below are given some suggestions as to what steps should be taken. In the first place, some means might be devised whereby the driller would obtain a rough figure for the amount of gas in the mud. If a sharp increase of gas is observed, he is forewarned. The addition of barytes is not a very good remedy. It increases the margin of safety, but it also increases the viscosity, and hence the tendency to gas-cut, and a vicious circle is apt to be established. It should be used only as a last resource. Every effort should be made to reduce the amount of the gas in the mud by lowering the viscosity and degassing. It is unfortunate that there appears to be no really efficient type of mud degasser available, and some research on this subject should be amply repaid. The most dangerous period is when the pipe is out of the hole. Before pulling out, the mud should be conditioned and the gas removed. Care should be taken to see that no fresh gas is entering the mud. A thin mud will greatly reduce the swabbing effect when pulling out. The above suggestions may be rather vague, but work along these lines should lead to the development of a sounder technique, and consequent decrease in the number of blow-outs.

Conclusions.

The system of control outlined in this paper is based on various assumptions and approximations the validity of which is open to question. This is inevitable in any practical system until our knowledge of mud increases. The main thing is to establish tests which are as comparative as possible and to keep full records of them and the results obtained. From these records information is gained and the system gradually improved. This, the author can say from experience, is not merely of theoretical interest, but yields definite practical results.

The value of good mud control is only now being fully realized. It is not merely a question of saving barytes, but of preventing blow-outs, and of preventing damage to producing sands by water infiltration; with deep holes it often means the difference between making hole or not making hole, or, with heaving shale, of making hole or losing it. There are many problems connected with these points to be solved, and time and money spent on them should be amply repaid.

The author's thanks are due to Messrs. Apex (Trinidad) Oilfields, Ltd., for permission to publish this paper, and to Mr. G. H. Scott for frequent help and advice.

Bibliography.

[1] "Evaluation of Rotary Drilling Mud," by P. H. Jones and E. C. Babson, *Oil Weekly*, 2.12.35.

[2] "Drilling Mud," *Trans. Min. and Geol. Inst. of India*, Vol. xxxii.

DISCUSSION.

THE CHAIRMAN (Mr. L. A. BUSHE (Apex)), congratulating Mr. Darley on a very interesting and valuable paper, said that apart from the scientific aspect of mud treatment there were several questions of a practical nature he would like to ask members to deal with during the discussion: How many fields were using the local I.P.T. viscometer as their standard field measure of viscosity? What limits of viscosity were allowed on the field? What percentage of sand was allowed in the muds, and were de-sanders used to any extent? What types of mud degassers were used?

Mr. Bushe also asked speakers to give some indication as to whether they thought it was worth while continuing with these meetings while the war was on, as they would note that very few members of the Institute were present that evening, and the Committee was not sure that it might not perhaps be better to let the local Branch lie dormant until such time as there was not such a pressure of work that it made the obtaining of papers almost an impossibility.

The Chairman then declared Mr. Darley's paper open for discussion.

MR. G. H. SCOTT (Apex) wished to add his congratulations to those of Mr. Bushe. The paper was, to his mind, one of the first that had actually tried to strike a balance between the purely scientific aspect of mud and the practical side. In this work Mr. Darley must be given all credit for having arrived at a basis for mud treatment which, although admittedly purely applicable to local conditions, did correlate the viscosity of the mud as measured by the driller in the field with the laboratory performance.

With reference to the case of cement-cut muds, the I.P.T. viscometer, owing to its rather considerable head, gave a very high rate of shear through the orifice; only a few days ago he had a case where the I.P.T. viscometer was only 22 seconds, but the thixotropy was so high that the mud would not even flow through the laboratory viscometer after shearing.

He would ask the author to enlarge on the importance of the colloidal index when wishing to get Schlumberger plummets to bottom or when running casing.

Mr. Scott referred to the question of variation in the size of hole. If one had changes in the size of the hole there was always the danger, especially in a deep hole, that the large hole above the pilot hole would ultimately build up to the diameter of the pilot hole. He believed Mr. Darley could give some actual cases of this.

As the author had pointed out, his use of the term "suspensoid" was perhaps a little unfortunate; "suspensoid" as used in pure colloidal chemistry was rather limited to the hydrophobic type of sol. He could think of no other term for particles which, although larger than colloidal dimensions, were held in suspension by the nature of the dispersive base and by their concentration.

With regard to the question of gas-cutting and blow-outs, Mr. Scott pointed out that the modern tendency to "slim" holes tended to aggravate the danger unless rigid mud control was observed. In many cases the interstitial gas in the sand actually excavated by the bit was sufficient to cause extensive gas-cutting. Furthermore, the tendency to swab a hole when pulling out was increased as hole diameters decreased, and it was of prime importance to condition the mud and secure a low viscosity prior to a "round trip."

MR. DARLEY, replying, said that with regard to the colloidal index when running Schlumberger plummets, it was a point that had to be taken very much into account. If you had a mud yielding quite a good viscosity at the well but having a high colloidal index, it was going to gel fast, and by the time the Schlumberger plummet got down it might be thick enough to prevent it reaching bottom. He had not done many experiments in this direction, but generally found that agents such as quebracho would reduce viscosity but did not greatly affect the rate at which the mud gelled. The only solution, he thought, was to dilute the mud down.

On the point of different sizes of hole, he thought perhaps the worst case was when cavities due to caving were obtained, resulting in changes of velocity which caused the deposition of cuttings.

Mr. G. S. Taitt (United British Oilfields of Trinidad) said he was interested in the Chairman's remarks with regard to the holding of meetings of the Branch. This was the first time he had had the opportunity of attending one himself, but he felt it would be a great pity if the meetings had to be given up, though he quite realized the difficulties under present conditions. He suggested it would be better to have an occasional paper—say once in one or two months—rather than close down the Branch altogether, because there was always a certain amount of initiative available.

He thought Mr. Darley was to be congratulated on the systematic way in which he had dealt with his particular mud problems.

In the first part of the paper, dealing with flow characteristics of mud, several references were made to the possibility of discounting the effect of thixotropy—*e.g.*, in measuring viscosities after an interval of not more than half a minute. However, the speaker had had some experience of muds gelling almost instantaneously, which had prevented the obtaining of accurate viscosities and comparative figures, so that he felt it could not be completely neglected. He did not know if Mr. Darley had come across such conditions.

He thought the importance of thixotropy had not perhaps been stressed enough in the paper, because even with mud which showed a very good condition while circulating, its thixotropy was of great importance; for example, if the pumps were shut down, even for a short time, when starting up again high initial pressure due to gelling might cause complete loss of circulation.

On the question of the colloidal index, tests might be made by preparing standard muds; but had Mr. Darley noticed the change which took place after a period of circulation with a given mud? They had observed that with some muds the clay content appeared quite satisfactory at the beginning, but after a while, possibly due to crushing or grinding of clay particles, the colloidal content appeared to have gone up.

In connection with the degassing of muds, had Mr. Darley had experience of vacuum degassifying?

With regard to plastering, Mr. Darley had stated in his paper: "Also it must be remembered that gas will tend to seep into the mud from sands already penetrated because of the difference in specific gravity between it and the mud. This will not be controlled by the difference in pressure between the gas and mud column but by the formation and maintenance of a good mud sheath on the face of the sand."

Some experiments had been made which tended to suggest that the pressure required to deplaster was very low indeed with a good mud, and therefore he wondered why Mr. Darley attached such importance to the nature of the mud sheath for holding back gas.

Mr. Darley, replying on the question of muds setting instantly due to thixotropy, said that he had, of course, had experience of such a condition. His actual remark had been made in connection with his tests of the rate of discharge against head. He was merely trying to establish the relationship and get some values for the Apex field. The muds used were all fairly thin muds, gelling effect was slight, and the actual motion through the viscometer was quite sufficient to prevent the thixotropy from having any effect. He quite agreed that with very thick muds of high thixotropy, viscometer readings were apt to be very seriously upset.

The change in viscosity due to circulation was very readily understandable. The point was well illustrated by the difficulty in obtaining a constant viscosity when making up a mud from the raw clay. His own standard muds were mixed by placing in a concrete mixer and rotating for a day, and even then, on putting them in the viscometer and rotating he could still get a rise in viscosity over a period of time. This was undoubtedly due to the particles of the clay becoming more and more dispersed and becoming finer; their surface area was increased and colloidal properties came more and more into play.

With regard to vacuum degassing, he had no field experience, but had tried it in a small way in the laboratory, just holding a small vacuum of a few inches. The difference he had obtained was practically negligible.

With regard to plastering, his answer to the question whether gas could seep into the mud against a higher head if there was not a mud sheath, was emphatically yes. Gas would tend to rise purely because it was lighter than the mud. If one had a

closed glass tube with mud in it and an air space at the top, and the tube was reversed end for end, the air bubble would go back to the top. The function of the mud sheath was that of a membrane to prevent that action. He had done no experiments on the force necessary to remove the mud sheath, but this must obviously be dependent on the difference between the reservoir pressure and the pressure of the mud column. That was where loading of the mud was of value.

Mr. Taitt explained that he realized the necessity for some mud sheath (which, he assumed, would be present in any case), but he wondered if Mr. Darley had noticed any difference with muds of different plastering qualities.

Mr. Darley replied that he had no comparisons from which conclusions could be reached.

Mr. N. Healey (United British Oilfields of Trinidad), speaking on the question of gas entering mud, said that when a sand had been drilled, if the hydrostatic head of the mud was higher than the reservoir pressure, laboratory experience showed that the absorptive effect would give rise to gas-cutting, even though there was a far greater pressure due to the mud than to the reservoir.

He also raised the point about the abrasiveness of particles in mud and particle size. He believed particle sizes had very little to do with abrasive action and it was much more due to particle shape. If you had sand particles which were perfectly rounded, there would be very little abrasive action indeed, but if they had sharp corners, even if of very small size, they would have considerable abrasive action. Laboratory experiments could be done with particles of different kinds.

Mr. Darley agreed that shape must have a very great deal to do with it, but, given the same shaped particles, the larger particles would give deeper scratches, smaller ones having more of a polishing effect.

Mr. Healey suggested, with regard to the colloidal index, that if a standard mud could be prepared—which was admittedly difficult—and some amount of standard clay and water put in and ground for some definite time, taking some standard clay such as Aquagel instead of local Trinidad clay, then perhaps one could get an almost universal standard mud, which would help in comparing muds in different countries.

Mr. Darley thought that this would be a very useful thing for comparing results between one field and another.

Mr. Scott remarked that bentonites were so liable to variation that he did not think Aquagel could be trusted any more than clay as a standard.

Mr. Darley stated that he had had samples of bentonites which had completely lost their gelling qualities merely with age. Therefore he did not think such a sensitive clay would be suitable for preparing a standard mud.

Mr. Healey mentioned the difficulty in correlating results on the rig with those obtained in the laboratory. With regard to viscosity, an even better criterion would be to take the pump pressure and rate of circulation. If there was streamline flow in the annulus, the laws of viscosity should apply, and from that it should be possible to get some idea of the viscosity. It would then remain to correlate this with the laboratory viscosity.

Mr. Darley pointed out that the trouble would be to standardize conditions. There were so many other important factors—*e.g.*, if a change was made from 4-inch to 2-inch drilling pipe, the pump pressures would almost double themselves.

Dr. A. J. Goodman (Cory Bros.) mentioned a mud degasser which he had seen in the *Oil Weekly* about two months previously.

Mr. Darley said he had recently come across one which had a vacuum at the top and baffles to increase the area exposed to the vacuum. He had not used anything similar to that.

Mr. Bushe said that the Committee hoped to have another paper late in June. If any member had a particular urge to read a paper before the Branch and would write to the Secretary, they would see what could be done about it.

In conclusion, he proposed a vote of thanks to Mr. Darley for his paper, and also to the Apex Club for the use of their Clubroom.

SYNTHESIS AND PROPERTIES OF MONO-NORMAL-ALKYLBENZENES.*

PART I.—METHODS FOR THE ALKYLATION OF BENZENE.

By G. Shen, M.Sc., A.M.Inst.Pet., T. Y. Ju, B.Sc., Stud.Inst.Pet., and C. E. Wood, M.Sc., A.I.C., F.Inst.Pet.

Synopsis.

The principal available methods for preparing alkyl (long-straight chain) benzenes are reviewed critically. Seven methods are considered in detail—namely, (1) Fittig's synthesis; (2) condensation of alkyl halides with benzene; (3) condensation of olefines with benzene; (4) condensation of alcohols with benzene; (5) interaction of inorganic and organic esters with benzene; (6) Grignard synthesis; and (7) hydrogenation of alkyl aryl ketones. Each reaction is considered and explained in electronic terms. Certain complicated reactions difficult of explanation on a logical basis and which lead to contradictory conclusions can be explained by, and are in agreement with, the fundamental ideas of activation and addition of an addend after cleavage in accordance with Markownikoff's rule. The first six methods are considered unsuited with regard to good yield and purity of the product.

The hydrogenation of alkyl aryl ketones prepared by the Friedel and Crafts' reaction (acylation of benzene) appears to be the best method for obtaining the large quantities of hydrocarbons which are necessary for the determination of cetane numbers. This process is on the whole of a simple character, not involving rearrangement of alkyl groups, and is unaccompanied by side reactions; further, the process does not involve a too-elaborate organic technique. Palladium is the best catalyst for carrying out the hydrogenation. Considering different chemical methods of reduction, the Clemmensen's method is to be preferred.

Numerous methods are available for the preparation of the mono-*n*-alkylbenzenes, and in a survey of the literature certain methods are difficult, others easy in technique. The yield of the product is, as a rule, low, and the pure hydrocarbon can be isolated only with difficulty. Thus, a comparative and critical study of all available methods mentioned in the literature has been made. Eight principal methods for the alkylation of the aromatic nucleus are in use :—

(1) Fittig's synthesis.

(2) Condensation of alkyl halides with benzene using aluminium chloride (Friedel and Crafts' reaction) or hydrogen fluoride.

(3) Condensation of olefines with benzene in the presence of hydrogen fluoride, sulphuric acid, aluminium chloride, ferric chloride, or phosphoric acid.

(4) Condensation of alcohols with benzene in the presence of boron trifluoride, aluminium chloride, phosphorus pentoxide, or boric acid (through the intermediate formation of R_3BO_3 from the corresponding alcohol, ROH, and boric acid) and aluminium chloride.

(5) Interaction of inorganic and organic esters with benzene in the presence of boron trifluoride, aluminium chloride, or hydrogen fluoride.

(6) Grignard synthesis.

(7) Hydrogenation of alkyl aryl ketones which may be prepared by the following principal methods :—

* Paper received 8th May, 1940.

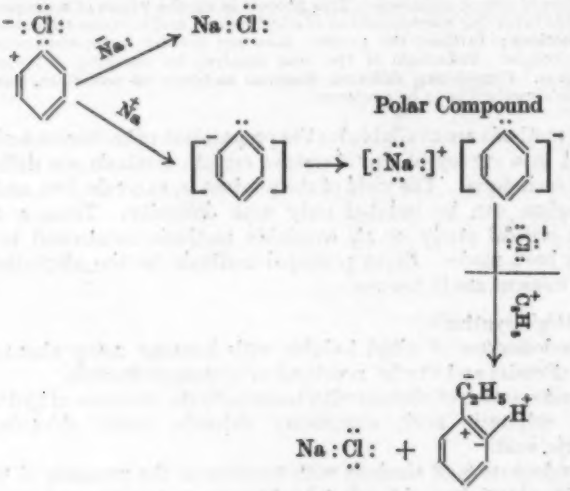
(*a*) Acylation of benzene by Friedel and Crafts' reaction.
(*b*) Grignard synthesis.
(*c*) Passing the vapours of benzoic and the fatty acids through heated manganous oxide or thorium oxide according to the elegant method of Sabatier.

(8) Reaction between *cyclo*propane and benzene using as catalyst hydrogen fluoride. The explanation of the reaction possibly involves an ionic mechanism (Simons, Archer, and Adams, *J. Amer. chem. Soc.*, 1938, **60**, 2955–2956).

It is interesting to review briefly the methods which have at times been utilized for this particular type of alkylation.

(1) *Fittig's Synthesis.*

The first stage in the accepted explanation of the Fittig reaction (Tollens and Fittig, *Annalen*, 1864, **131**, 303) is the formation of sodium phenyl, C_6H_5Na (Acree, *Amer. Chem. J.*, 1903, **29**, 588; Schlubach, *Ber.*, 1922, **55**, 2889), on the immediate liberation of the phenyl radical. The second stage involves the reaction of sodium phenyl with the alkyl or aryl halide in accordance with the following explanation, in which it is interesting to note the amphoteric character of carbon :—



The polar compound reacts more readily with the alkyl halide than with the aryl halide, and on this account the yield of alkylated benzene is much better than would be anticipated in view of the three possible products. Butylene, butane (both formed from the free radicals), and diphenyl are by-products. Sodium is the metal most useful for coupling alkyl and aryl radicals. Bachmann and Clarke (*J. Amer. chem. Soc.*, 1927, **49**, 2089) found that the action of sodium on chlorobenzene at the boiling point gave benzene, diphenyl, *o*-diphenylbenzene, triphenylene, 2 : 2-diphenyl-

diphenyl and resinous tars; further, the action of sodium on *n*-heptyl bromide gave *n*-heptane, heptylene, tetradecane, heneicosane, and high-molecular-weight hydrocarbons. Copper, however, is most suited for this type of coupling.

n-Amylbenzene was prepared by Schramm (*Annalen*, 1883, **218**, 388) by action of sodium on a mixture of benzyl bromide and butyl bromide. The yield was about 25 per cent. theoretical, dibenzyl and *n*-octane and some unidentified hydrocarbons being formed at the same time. Radcliffe and Simpkin (*J. Soc. chem. Ind.*, 1921, **40**, 119–122T) use benzyl chloride instead of benzyl bromide, and the yield is similar to that obtained by using benzyl bromide, but requires a longer time for completion of the reaction. *n*-Amylbenzene was also prepared by Radcliffe and Simpkin (*loc. cit.*) by treating a mixture of phenyl bromide and amyl bromide with metallic sodium, the yield being two to three times greater.

Possible combinations of organo-sodium compounds and organic chlorides in the Fittig's synthesis of *n*-amylbenzene have been studied recently by Morton and Fallwell (*J. Amer. chem. Soc.*, 1938, **60**, 1429–1431). The yield was low (5–11 per cent.). However, a better yield (54–70 per cent.) was obtained by using sodium benzyl instead of sodium phenyl.

In view of these side reactions, which, in certain circumstances, might well overwhelm the required synthesis, the Fittig reaction is not satisfactory for preparing long-chain benzene homologues, the isolation of which in the pure condition from complex by-products entails elaborate technique with consequent diminution in yield.

(2) *Condensation of Alkyl Halides with Benzene in the Presence of Aluminium Chloride or Hydrogen Fluoride.*

Friedel and Crafts (*Compt. rend.*, 1877, **84**, 1392, 1450; cf. Ashdown, *Industr. Engng Chem.*, 1927, **19**, 1063) synthesized amylbenzene using amyl chloride; the hydrocarbon, however, had b.p. 185–190°. According to recent literature, *n*-amylbenzene has b.p. 205·3° (Simon, *Bull. Soc. chim. Belg.*, 1929, **38**, 47) and the tertiary compound boils at 190° (Verley, *Bull. Soc. chim.*, 1898, (3), **19**, 67; Tzukervanik, *J. Gen. chem. U.S.S.R.*, 1935, **5**, 117). This indicates either that the amyl chloride used by Friedel and Crafts was not the pure normal compound, or, if such was employed, then rearrangement of the *n*-amyl group had taken place in the reaction. Simon and Archer (*J. Amer. chem. Soc.*, 1938, **60**, 2953) obtained only fair yields of the alkylated benzenes by using hydrogen fluoride. From *n*-propyl bromide a 48 per cent. yield of propylbenzenes (containing 88 per cent. *iso*propyl and 12 per cent. *n*-propyl) and from *tert.*-amyl chloride a 41·5 per cent. yield of mono-*tert.*-amylbenzene were obtained. The following shows the ease of rearrangement of the halides :—

Temperature.	Halide.	Product.
—	*n*-Propyl halide	*iso*Propylbenzene predominates.
0°	*n*-Butyl halide	*n*-Butyl- and *sec.*-butyl benzene.
Higher temperature than 0°	*n*-Butyl halide	*sec.*-Butylbenzene.
As low as −18°	*iso*Butyl halide	*tert.*-Butylbenzene exclusively.
—	*iso*Amyl halide	*iso*Amylbenzene and *tert.*-amylbenzene.

The reaction is considered below in terms of electronic structures :—

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl + AlCl_3 \longrightarrow [CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\overset{+}{Cl} - \overline{AlCl_3}]$$

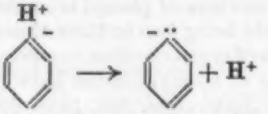
This reaction is catalytic—*i.e.*, no stable organo-aluminium compound is formed :—

$$[CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2\overset{+}{Cl} - \overline{AlCl_3}] \longrightarrow CH_3{\cdot}CH_2{\cdot}CH = CH_2 + HCl + AlCl_3$$

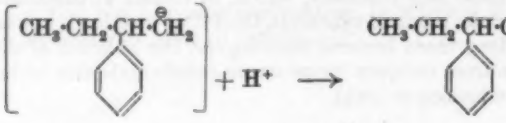
Activation of unsaturated hydrocarbon :—

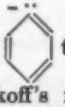
$$CH_3{\cdot}CH_2{\cdot}CH = CH_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}\overset{\oplus}{C}H - \overset{\ominus}{C}H_2$$

Dissociation of proton from benzene ring :—



Then addition of the phenyl radical to the activated hydrocarbon to give the *iso*alkylated benzene after proton addition :—



The addition of proton H^+ and phenyl  to the unsaturated hydrocarbon is in accordance with Markownikoff's rule (*Annalen*, 1870, **153**, 256; *Compt. rend.*, 1875, **81**, 670). The reaction *is not* the breaking down of an activated covalent alkyl halide into ions

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Cl \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2^+ + Cl^-$$

then dissociation of a proton from the benzene nucleus and addition of the alkyl radical to the residual phenyl grouping, this would lead to the formation of a *normal*-alkylated benzene.

The cleavage of the halide has been investigated by H. Gilman and R. R. Burtner (*J. Amer. chem. Soc.*, 1935, **57**, 909) in the furan series, the *tert.*-butyl derivative having been obtained from each of the following : *n*-hexyl bromide, *n*-octadecyl bromide, and *n*-amyl chloride.

The control of conditions for introducing an alkyl group is easy, but there is possible rearrangement and cleavage of the *n*-alkyl group.

The use of *n*-alkyl halide (particularly of higher *n*-halides) for the preparation of mono-*n*-alkylated benzenes was therefore not practicable.

It is to be noted that Norris and Rubinstein (*J. Amer. chem. Soc.*, 1939, **61**, 1163–1170) obtained *s.*-triethylbenzene in 85–90 per cent. of the theoretical from ethylation of benzene with ethyl chloride and ethyl bromide when the molecular ratio of aluminium chloride to benzene was 1 : 1. The methylation of benzene with 3 moles of methyl halide gives 1 : 2 : 4-trimethylbenzene at 0° and 1 : 3 : 5-trimethylbenzene at 100°.

(3) *Condensation of Olefines with Benzene.*

The condensation of olefines with benzene in the presence of various condensing agents gives the same products as those obtained from the corresponding alkyl halides.

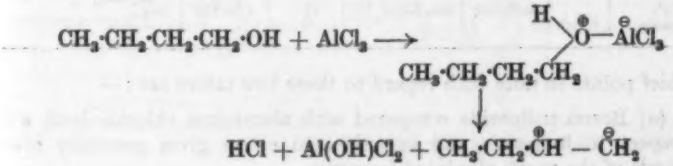
Olefine.	Condensing agent.	Product.	Reference.
Propene	$AlCl_3$	*iso*Propylbenzene	Berry and Reid (*J. Amer. chem. Soc.*, 1927, **49**, 3142).
,,	BF_3	,,	Slanina, Sowa, and Nieuwland (*ibid.*, 1935, **57**, 1547).
n-Butene	BF_3	*mono*Butylbenzene isomers	*Ibid.*
Propene	HF	84% yield *iso*propylbenzene	Simon and Archer (*ibid.*, 1938, **60**, 2952).
*iso*Butene	HF	44% yield mono-*tert.*-butylbenzene and poly-alkylated benzenes	*Ibid.*
,,	96% H_2SO_4	77% yield *p*-di-*tert.*-butylbenzene and small percentage of mono- and tri-derivatives	Ipatieff, Corson, and Pines (*ibid.*, 1936, **58**, 919).
*iso*Pentene	96% H_2SO_4	20% *tert.*-amylbenzene 56% diamylbenzene	Ipatieff, Pines, and Schmerling (*ibid.*, 1938, **60**, 353).
tert.-Pentene	96% H_2SO_4	18% *tert.*-amylbenzene 50% di-*tert.*-amylbenzene	*Ibid.*
Propene	$FeCl_3$	91% *iso*propylbenzene	Potts and Carpenter (*ibid.*, 1939, **61**, 663).
*iso*Butene	$FeCl_3$	89% *tert.*-butylbenzene	*Ibid.*
,,	P_2O_5	*tert.*-Butylbenzene	Malishev (*ibid.*, 1935, **57**, 883).
Olefines from cracked gasoline and kerosine.	$AlCl_3$	Mono-alkylated benzenes (structure of alkyl groups apparently not investigated)	Tilicheev and Kuryndin (*Neft. Khoz.*, 1930, **19**, 596).
Olefines (sources as above)	$FeCl_3$	68% yield mono-alkylated benzenes (alkyl groups not normal)	Kuryndin, Voevodova, and Rasskazova (*J. appl. Chem. (U.S.S.R.)*, 1937, **10**, 877).

Ipatieff, Pines, and Komarewsky (*Industr. Engng Chem.*, 1936, **28**, 222) have used phosphoric acid as condensing agent.

In this case (3), also, the addition of benzene to the olefine takes place according to Markownikoff's rule. Similar remarks as made under (2) apply here. The preparation of *n*-alkylated benzenes in reasonable yield under investigated conditions is impossible.

(4) *Condensation of Alcohols with Benzene.*

In the condensation of alcohols with benzene (in the presence of dehydrating agents as BF_3, $AlCl_3$, P_2O_5, H_2SO_4, etc.) *sec.*- and *tert.*-alkylbenzenes are obtained. The reaction proceeds with the intermediate formation of the olefine (cf. Tzukervanik, *J. Gen. Chem., U.S.S.R.*, 1935, 5, 117) and then addition of benzene as explained above. Taking *n*-butyl alcohol as an instance, the first two stages of the reaction may be represented thus :—



The following table shows the products of alkylation.

Alcohol.	Condensing agent.	Product.	Reference.
n-Propyl	BF_3	*iso*Propylbenzene	McKenna and Sowa (*J. Amer. chem. Soc.*, 1937, **59**, 470).
*iso*Propyl	,,		
n-Butyl	BF_3	*sec.*-Butylbenzene	
sec.-Butyl	,,		
*iso*Butyl	BF_3	*tert.*-Butylbenzene	
tert.-Butyl	BF_3	,,	
*iso*Propyl	80% H_2SO_4	*iso*Propylbenzene and poly-substitutes	Meyer and Bernhauer (*Monatsh.*, 1929, **53–54**, 721).
n-Butyl	H_2SO_4	*sec.*-Butylbenzene and di-substitutes	*Ibid.*
*iso*Butyl	H_2SO_4	*tert.*-Butylbenzene and di-substitutes	*Ibid.*
tert.-Butyl	H_2SO_4	*tert.*-Butylbenzene and di-substitutes	*Ibid.*
Methyl	$AlCl_3$	21% yield toluene	Norris and Sturgis (*J. Amer. chem. Soc.*, 1939, **61**, 1413).
Ethyl	$AlCl_3$	50% yield ethylbenzene	*Ibid.*
*iso*Propyl	$AlCl_3$	*iso*Propylbenzene	Huston and Haich (*ibid.*, 1936, **58**, 439).
,,	$AlCl_3$	*iso*Propylbenzene and ethylbenzene	Norris and Sturgis (*loc. cit.*).
tert.-Butyl	$AlCl_3$	84% *tert.*-butylbenzene	*Ibid.*
,,	$AlCl_3$	67% *tert.*-butylbenzene	Huston and Haich (*loc. cit.*).

The disadvantages of using alcohols are similar to those of using olefines or alkyl halides. In reactions (2) and (3) the $AlCl_3$ or other condensing reagent employed reacts catalytically; in (4), however, $AlCl_3$ (P_2O_5, H_2SO_4, etc.) dehydrates and then the excess $AlCl_3$ acts as a powerful catalyst.

(5) *Interaction of Inorganic and Organic Esters with Benzene.*

The reagents used to promote the condensations are BF_3, HF, and $AlCl_3$. Some recent results are tabulated below.

TABLE I.

Ester Inorganic.	Condensing agent.	Temp. (highest), °C.	Nature of alkyl group in benzene.	% yield of mono-alkylated benzenes.	B.p. of mono-alkylated benzenes, °C.	Reference.
1. *n*-Propyl-sulphate	BF_3	Refluxed	*iso*Propyl	45	—	McKenna and Sowa (*J. Amer. chem. Soc.*, 1937, **59**, 1204).
2. *iso*Propyl-sulphate	,,	,,	,,	38	—	*Ibid.*
3. *n*-Butyl-phosphate	,,	,,	*sec.*-Butyl	11	—	*Ibid.*
4. Diethyl-sulphate	$AlCl_3$	70°	Ethyl	71·4	133–137°	Kane and Lowy (*J. Amer. chem. Soc.*, 1936, **58**, 2605).
5. Dibutyl-sulphate	,,	70°	Isomeric mixtures of butyl benzenes	43·6	165–175°	*Ibid.*
6. *n*-Propyl-sulphite	,,	60°	*n*-Propyl	66	150–151°	Everett Bowden (*J. Amer. chem. Soc.*, 1938, **60**, 645).
7. *n*-Butyl-sulphite	,,	Refluxed	*sec.*-Butyl	41	170–172°	*Ibid.*

The chief points to note with regard to these two tables are :—

(*a*) Boron trifluoride compared with aluminium chloride both with respect to inorganic and organic acid esters gives generally lower yields of the mono-alkylated benzenes.

(*b*) Using BF_3 (1) the *iso*- or *sec.*-alkylated benzenes are obtained from the *n*-alkyl ester (cf. *n*-propyl and *n*-butyl esters); (2) the mono-*tert.*-alkylated benzenes are obtained from the *iso*alkyl ester.

(*c*) Aluminium chloride gives *normal* and not *iso*propylbenzene under the standardized conditions of the authors mentioned.

TABLE II.

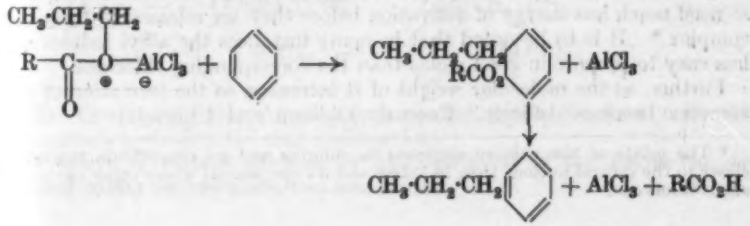
Ester organic.	Condensing agent.	Temp. (highest), °C.	Nature of alkyl group in benzene.	% yield of mono-alkylated benzenes.	B.p. of mono-alkylated benzenes, °C.	Reference.
1. *n*-Propyl formate	BF_3	Refluxed	*iso*Propyl	33·4	—	McKenna and Sowa (*J. Amer. chem. Soc.*, 1937, **59**, 1204).
2. *iso*Propyl acetate	,,	,,	,,	16·4	—	*Ibid.*
3. *n*-Butyl formate	,,	,,	*sec.*-Butyl	33·2	—	*Ibid.*
4. *iso*Butyl formate	,,	,,	*tert.*-Butyl	30·6	—	*Ibid.*
5. *sec.*-Butyl formate	,,	,,	*sec.*-Butyl	26·0	—	*Ibid.*
6. *sec.*-Butyl acetate	,,	,,	,,	29·6	—	*Ibid.*
7. *n*-Propyl formate	$AlCl_3$	60°	*n*-Propyl	66	150–151°	Everett Bowden (*J. Amer. chem. Soc.*, 1938, **60**, 645).
8. *n*-Butyl formate	,,	75°	*sec.*-Butyl	73	170–172°	*Ibid.*
9. *iso*Propyl acetate	,,	Refluxed	*iso*Propyl	68	148–148°	*Ibid.*
10. *iso*Butyl acetate	,,	60°	*tert.*-Butyl	33	168·5°	*Ibid.*
11. *iso*Propyl acetate	HF	80–100°	*iso*Propyl	53	149–150/ 742 mm.	Simons, Archer, and Randall (*J. Amer. chem. Soc.*, 1939, **61**, 1821–1822).
12. *n*-Butyl acetate	,,	80–100°	*sec.*-Butyl	60	170·5–171/ 742 mm.	*Ibid.*
13. *sec.*-Butyl *iso*butyrate	,,	80–100°	,,	56	170–171/ 742 mm.	*Ibid.*
14. *tert.*-Butyl acetate	,,	80–100°	*tert.*-Butyl	71	170–171/ 742 mm.	*Ibid.*

(*d*) Aluminium chloride reacts in the usual manner to give *sec.*- and *tert.*-butylbenzenes from *n*- and *iso*-butyl esters, respectively.

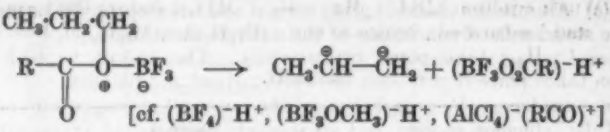
(*e*) Hydrofluoric acid acts similarly to boron fluoride.

(*f*) No rearrangement takes place on using either BF_3 or $AlCl_3$ with regard to the *iso*propyl radical or on using BF_3 with regard to the *sec.*-butyl radical.

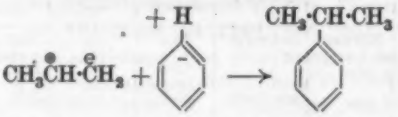
A mechanism similar to the Friedel and Crafts' reaction may be postulated for these esters on using aluminium chloride. Co-ordination with the oxygen of the ester grouping occurs, followed by addition of the alkyl radical and the residual complex at the double bond of the aromatic ring, then the elimination of the acid.



which virtually amounts to the addition of the ions activated $C_3H_7^+$ and $R{\cdot}CO_2^-$ at the double bond. Co-ordination of BF_3 results apparently in olefine formation :—



then prototropic change and addition take place :—



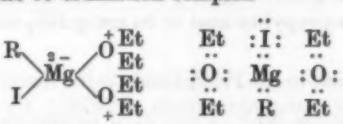
In the case of (*a*), the normal butyl esters and $AlCl_3$ or BF_3, the intermediate is activated butene-1 ($CH_3{-}CH_2\overset{+}{C}H{-}\overline{C}H_2$), which forms *sec.*-butylbenzene; (*b*), the *sec.*-butyl esters and BF_3, the intermediate is activated butene-2 ($CH_3{\cdot}\overset{+}{C}H{-}\overline{C}H{\cdot}CH_3$), which forms *sec.*-butylbenzene; (*c*), the *iso*butyl esters and $AlCl_3$ or BF_3, the intermediate is activated methylpropene $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\overset{+}{C}{-}\overline{C}H_2\right)$, which forms *tert.*-butylbenzene.

In all cases the hydrogen (Proton) or "positive" part of the benzene nucleus adds to the end carbon atom ($-CH_2$ or $-CH-$) (Markownikoff's rule).

So far as is known, no normal alkylated benzenes (higher than propyl) can be formed by methods (2), (3), (4), and (5), although the known reversal of Markownikoff's rule (addition of haloid acid to olefines in the presence of peroxides) would indicate the possibility of their formation under modified conditions.

(6) *The Grignard Synthesis.*

The formation of the co-ordination complex



proceeds more easily with alkyl or aryl *iodides* than with other halides, for the valency electrons of the iodide ion move under the action of much weaker fields than the valency electrons of the chloride or fluoride ion, and so need much less energy of activation before they are released to form the complex.* It is to be noted that in many instances the alkyl iodides are less easy to prepare in good yields than the corresponding chlorides.

Further, as the molecular weight of R increases, so the formation of the complex becomes difficult. Recently Oldham and Ubbelohde (*J. chem.*

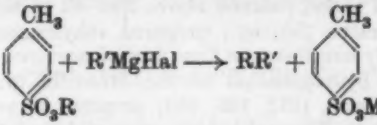
* The orbits of the valency electrons in chlorine and its compounds are much closer to the central nucleus than in iodine and its compounds where other electronic shells intervene.

Soc., 1938, 201) investigated the products of the reaction of various higher-molecular-weight halides on magnesium in the presence of ether. They showed that the three reactions (*a*) formation of the Grignard complex, (*b*) the Wurtz reaction ($2RI + Mg = R_2 + MgI_2$), and (*c*) the formation of olefine and saturated hydrocarbon ($C_{12}H_{25}I + C_{12}H_{25}MgI = MgI_2 + C_{12}H_{24} + C_{12}H_{26}$) take place concurrently. The extent to which each reaction takes place depends on the alkyl radical and halogen.

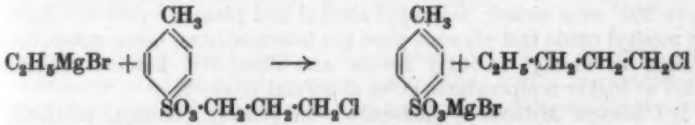
Even considering the preparation of the lower alkyl magnesium complex, C_2H_5MgBr, efficient cooling and stirring are essential to prevent the side reaction: $2C_2H_5Br + Mg \longrightarrow C_2H_4 + C_2H_6$, which is favoured by rapid addition of the bromide and by too small a concentration of ether (Wood and Scarf, *J. Soc. chem. Ind.*, 1923, **42**, No. 2, 13T).

Thus the Grignard reagent with higher alkyl halides gives higher hydrocarbons in poor yields only, such reactions being used as a last resort.

On the other hand, interaction between RMgBr and C_6H_5Br gives diphenyl if the reaction goes too violently. Considering the following reaction, $RHal + R'MgHal \longrightarrow MgHal_2 + RR'$ the yields are poor, particularly with tertiary halides. A modification which gives better yields involves the use of aromatic sulphonic acid alkyl esters :—



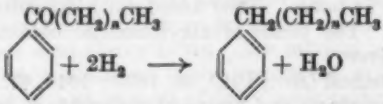
It should be mentioned, however, with regard to the use of alkyl halides in other types of synthesis, that the chain of an alkyl halide may be lengthened by three carbon atoms by treating its Grignard reagent with γ-chloropropyl-*p*-toluenesulphonate :—



This alkyl halide can now be used in hydrocarbon synthesis.

(7) *Hydrogenation of Alkyl Aryl Ketones.*

The controlling of the hydrogenation of the ketone to the second stage —viz., the aryl hydrocarbon—is one requiring considerable experience of hydrogenation technique :—



The first stage yields the secondary alcohol, whilst the final yields the completely hydrogenated ring hydrocarbon.

A study of certain methods of hydrogenation of the ketone to the corresponding aryl hydrocarbon was made.

(a) *Palladium as Catalyst.*—Hartung and Crossley (*J. Amer. chem. Soc.*, 1934, **56**, 158) reduced ethyl phenyl ketone in alcoholic solution to propylbenzene, using palladinized animal charcoal which was prepared according to the direction of Otto and Schroeter (*Ber.*, 1927, **60**, 633). The method was claimed to be successful for the complete intermediate reduction of ketone to hydrocarbon without the formation of secondary alcohol or alkyl*cyclo*hexane.

(b) *Platinum-black as Catalyst.*—Vavon (*Compt. rend.*, 1912, **155**, 286) hydrogenated acetophenone in 60 per cent. aqueous alcohol, giving almost pure methylphenylcarbinol. In ether, alcohol (absolute), ethyl acetate, or acetic acid, however, the product was ethyl*cyclo*hexane. So the control of the second hydrogenation stage is rendered very difficult.

(c) *Nickel as Catalyst.*—The activity of catalytic nickel depends on the method of preparation. The temperature used for reduction of the oxide is an important factor. Darzens (*Compt. rend.*, 1904, **139**, 869) and Brunel (*Ann. Chim. Phys.*, 1905, **6**, (8), 205) found that the higher the temperature of reduction the feebler was the activity of the resulting nickel; hence hydrogenation of the benzene nucleus is slow with catalyst prepared above 300° C.

In the presence of nickel reduced above 300° C. of moderate activity at 190–195° C., Darzens (*loc. cit.*) prepared ethylbenzene from acetophenone and similarly butylbenzene from benzyl acetone. A more active catalyst causes the hydrogenation of the aromatic nucleus. Sabatier and Murat (*Compt. rend.*, 1912, **155**, 385) prepared di*cyclo*hexylpropane, $C_6H_{11}(CH_2)_3C_6H_{11}$, from dibenzyl ketone using nickel at 175°. At higher temperatures—*i.e.*, at 250–300° C.—Haller and Lassieur (*Compt. rend.*, 1910, **150**, 1013) hydrogenated methyl nonyl ketone using nickel, and obtained nonane, C_9H_{20}, a pinacone, $C_9H_{19}C(CH_3)_2.CO{\cdot}C_9H_{19}$, and other products. Further, Lassieur (*Compt. rend.*, 1913, **156**, 795) reduced acetone above 200° over nickel; *iso*propyl alcohol and pinacone were not formed, but mesityl oxide and phorone were the intermediates, being subsequently reduced to methyl *iso*butyl ketone and di*iso*butyl ketone. Therefore nickel at higher temperatures gives abnormal products.

(d) *Chemical Methods of Reduction.*—In general, chemical methods of reduction of ketones give poor yields of alcohol or hydrocarbon, due to side reactions. For instance, with sodium or aluminium amalgam an aliphatic ketone is reduced to the corresponding secondary alcohol and a pinacone which may be the chief product.

Ziegler, Dersch, and Wollthan (*Annalen*, 1934, **511**, 13) prepared alkylbenzenes from alkyl aryl ketones by the Kishner–Wolf method of reduction. The semicarbazone is heated with sodium in absolute alcohol at 180° C. in an autoclave for 14 hours. They found much difficulty in the reduction of higher ketones. The yields of alkylbenzenes obtained, except amylbenzene, are not given.

Clemmensen's method (*Ber.*, 1913, **46**, 1838; 1914, **47**, 683) of reduction by means of zinc amalgam and hydrochloric acid is in general use for the preparation of hydrocarbons from ketones. Simon (*Bull. Soc. chim. Belg.*, 1929, **38**, 47), using Clemmensen's method, obtained amyl- and hexylbenzenes in 54 per cent. theoretical yield.

In view of the above, it may be concluded that palladium is the best

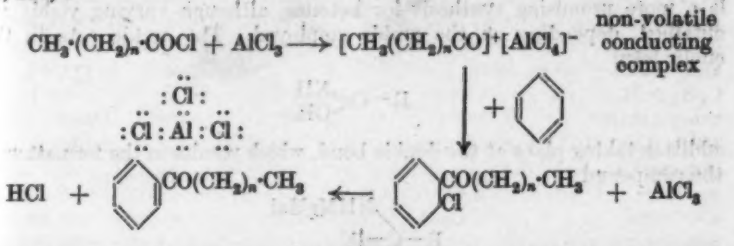
catalyst and in chemical methods zinc amalgam is the best reducing agent. Both methods are being used in this laboratory for the reduction of alkyl aryl ketones.

Methods for the Preparation of Alkyl Aryl Ketones.

Alkyl aryl ketones of higher molecular weight are not listed. The methods employed for their preparation are numerous. Certain of these methods are compared below.

(a) *Acylation of Benzene by Friedel and Crafts' Reaction.*—Acylation by this process is a very reliable method with no rearrangement of alkyl group; this stability of the addend is readily understood on consideration of the mechanism given below. It is applicable to a variety of reactants (cf. Galloway, *Chem. Rev.*, 1935, **17**, 327).

The co-ordinate compound of the acyl chloride and aluminium chloride initially interacts with the aromatic hydrocarbon at the double bond, which addition is immediately succeeded by the elimination of hydrochloric acid; further, the aluminium chloride forms a stable addition compound with the product of the reaction. In other words, the aluminium chloride labilizes the chlorine initially (cf. Schaarschmidt, *Z. angew. Chem.*, 1924, **37**, 286) :—



Simons, Randall, and Archer (*J. Amer. chem. Soc.*, 1939, **61**, 1795–1796) have demonstrated the effective use of hydrofluoric acid in the synthesis of ketones from aromatic compounds and carboxylic acids, anhydrides, and acyl halides. The yields increase with increasing amounts of hydrofluoric acid.

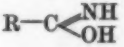
(b) *Method Employed by Sabatier.*—Sabatier and Mailhe (*Compt. rend.*, 1914, **158**, 830) prepared a series of alkyl aryl ketones by passing a mixture of the fatty and benzoic acids in the vapour phase over manganous oxide at 400–450° C. The method is only convenient for preparing ketones of lower molecular weight, on account of the higher fatty acids vaporizing with difficulty. The physical data recorded for *n*-octyl phenyl ketone prepared by Sabatier and Mailhe from pelargonic acid, however, are not in agreement with our own observations. The method is closely related to the classical method (Williamson) of the preparation of ketones by distillation of the calcium or barium salts of fatty acids under reduced pressure. Sabatier in his work "La Catalyse" mentions the catalytic formation of mixed ketones by the elimination of carbon dioxide from benzoic acid and lauric acid or myristic acid or stearic acid, or even phenyl acetic acid using thoria or manganous oxide as catalyst. The formation of three

ketones and their separation present difficulty in obtaining a particular ketone in a pure condition.

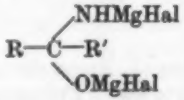
(c) *Grignard Synthesis of Ketones.*—The interaction of acyl anhydrides and alkyl magnesium halides to produce ketones has been the subject of extensive investigation. Ketones are produced in addition to tertiary alcohols. Again, by the carefully regulated action of magnesium complexes on acid chlorides and vice versa it is possible to prepare ketones, but here the reaction is not sufficiently controllable to give ketones in good yields (Nicholas and Wood, Investigation, Birmingham University). In explanation, it may be stated that the *negative* hydrocarbons ions, alkyl or aryl ($\overline{\text{alkyl}} + \overset{+}{\text{MgHal}}$), attach themselves readily to the positively polarized atoms of carbon of the carboxyl group

resulting in the easy formation of a tertiary alcohol. In both these cases it is difficult to stop at the intermediate ketone stage.

Possibly the action of acid amides on an excess of the Grignard reagent is a more promising synthesis for ketones, although varying yields are obtained, depending on the amide employed. The amide acts in the enolic form



addition taking place at the double bond, which results in the formation of the compound



which on treatment with acid or water readily decomposes to give the ketone.

This reaction should be investigated further; although there is a limitation to the chain length of R in formation of the Grignard reagent R–Mg–I and the use of the iodide is preferable. (As R increases, so the yield of the magnesium compound decreases, with simultaneous formation of olefine and saturated hydrocarbon.)

Yet the use of stearamide and palmitamide (cf. Ryan and Nolan, *Proc. Irish Acad.*, 1912, **30**, 1) to form ketones opens up the possibility of the formation of *long* straight-chain or branched-chain ketones, and hence of straight-chain or branched-chain paraffins of definite constitution.

The use of nitriles of the type of benzonitrile C_6H_5CN is also possible, but with nitriles of the type of benzyl cyanide, $C_6H_5CH_2CN$ (which approximates in properties to an aliphatic nitrile), much poorer yields are obtained.

Thus the length of the chain $C_6H_5(CH_2)_nCN$ attached to the benzene nucleus, both in this respect and also with respect to the methods of preparation of such semi-aryl cyanides, is strictly limited.

Other methods—for instance, the action of carbon dioxide under certain conditions on the Grignard reagent and the action of organo-magnesium halides on anilides and free acids—have been surveyed, but are not favourable for good yields of ketones of the type required in this investigation. It is difficult to arrest the reaction at the formation of ketone stage.

It is important to note that the *normal* action of a zinc organo-metallic compound on an acid chloride results in ketone formation with good yields :—

$$R{\cdot}COCl + Zn\langle{}^{R'}_{I} \longrightarrow RCOR' + Zn\langle{}^{Cl}_{I}.$$

The authors wish to thank Professor A. W. Nash for his continued interest in this work, which is being published in three papers. He has given every facility for the carrying out of the research and the authors are grateful to him.

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OBITUARY.

VICTOR HENNY.

Dr. Victor Henny, European representative of Universal Oil Products Company, died at his home near London, on 12th July, 1940. He was born at Salatiga, Java, in 1887, and was educated in Switzerland. He attended the Technical University at Zurich from 1906 to 1910, obtaining a degree in chemical engineering. Three years later he gained the degree of Doctor of Science in Chemistry at the same university.

After leaving Zurich, Dr. Henny joined the staff of the N.V. de Bataafsche Petroleum Co. in Holland, and for two years was Acting Refinery Manager of the benzine installation of this company at Rotterdam. In 1915 his services were loaned by the Royal Dutch-Shell to England, and he worked under the late Sir William J. Pope, at Cambridge, on the production of toluene and mononitrotoluene from special Borneo benzine. Later he was Works Chemist and Works Manager at H.M. Factory at Sandycroft. In 1919 and 1920 he managed the Portishead Refinery of the Asiatic Petroleum Co., and was then sent to California, where he worked in the Shell Refinery at Martinez. Throughout this period he was making an intensive study of cracking processes in U.S.A.

In 1924 he returned to London and was placed in charge of the activities of the Universal Oil Products Company in Europe, Asia, Africa, and British Colonies. His early scientific education and refinery experience, together with his extensive knowledge of the languages and customs of various countries, aided by a rare charm of manner, made him exceptionally suitable for this appointment. Thus, he was able to develop rapidly the cracking of oils in Europe by the Dubbs process. From the first unit built at Cernavoda for the Omnium International de Pétrole in 1925, of 500 barrels, to the time of his death, some 100 units, of approximately 285,070 barrels daily capacity, with 41 licensees, were installed.

Dr. Henny took an active interest in the Institute of Petroleum, of which he was a Fellow. In addition, he was a Fellow of the Institute of Fuel, a Member of the American Chemical Society, a member of the American Chamber of Commerce and the Dutch Club. In recent months he was much concerned about the fate of the country of his birth, and he participated actively in the forming and direction of the work of the Netherlands Emergency Committee. Only three weeks before his untimely death he was presented to Queen Wilhelmina as a result of his work in this latter connection.

Dr. Henny leaves a widow and four children, to whom go the sincere condolences of all who knew him. The library of scientific books which Dr. Henny had accumulated during his career has been generously presented to the Institute of Petroleum by Mrs. Henny.